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DENSIFICATION OF LMH-2 (U)

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ETHYL CORPORATION
Baton Rouge, La.

TECHNICAL REPORT AFRPL-TR-66-293

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> GROUP 4
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AIR FORCE ROCKET PROPULSION LABORATORY

RESEARCH AND TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

EDWARDS AIR FORCE BASE, CALIFORNIA

EC-924

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EC-924

(U) FOREWORD

This is the first quarterly report in partial fulfillment of Contract AF04(611)-11411 covering work performed during the period May 2 to July 29, 1966. The contractor was Ethyl Corporation, P. O. Box 53091, Baton Rouge, Louisiana 70805.

The work was performed under the supervision of Dr. F. W. Frey as Program Manager. Mr. E. M. Marlett served as Responsible Scientist, and Dr. G. J. Brendel as Research Chemist.

The program was sponsored by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards Air Force Base, California. The project engineer was 1st Lt. John Rombouts.

Ethyl Corporation EC-924 has been assigned by the contractor to identify this report.

Publication of this report does not constitute Air Force approval of the report findings or conclusions. It is published only for the exchange and stimulation of ideas.

(C) <u>ABSTRACT</u>

Ultra-high pressure hydrostatic equipment was obtained for use in BeH_2 crystallization studies. During its installation the crystallization of high-purity Li-doped BeH_2 (96 wt % BeH_2, 1.3 wt % Li) was investigated using an improved design piston-mold apparatus. The high purity feed material tended to give products with relatively high concentrations of crystalline Phase 338-208 and densities in the range 0.75 - 0.77 g/cc. As the pressure and temperature was increased, Phase 378-295 formed preferentially, as expected. Its density approached a value of 0.80 - 0.82 g/cc. Rate of temperature quench under pressure had no effect on extent of crystallization or polymorph distribution. On the other hand, a rapid pressure quench at elevated temperature is detrimental to the crystallization process. It was found that amorphous BeH_2 can be prepared in a fused, glassy state by pre-compaction, then heating without pressure to 170 - 200°C.

Investigation of impurities in BeH_2 showed that the presence of butoxide groups in the pyrolysis feed, di-_t_-butylberyllium etherate, enhanced the thermal stability of the _t_-butyl groups. This information aided the production of the highest purity Li-doped BeH_2 obtained to date. Attempts to improve purity even further by hydrogenolysis of residual alkyl groups proved unsuccessful.

(C) <u>TABLE OF CONTENTS</u>

(C) INTRODUCTION

Beryllium hydride (BeH_2) has the highest potential performance of any solid propellant fuel presently known. Interest in this fuel has continued to rise with progress in propellant development programs. Firing tests with solid grains have resulted in delivered impulses exceeding the goal of 280 seconds.[1] However, the beryllium hydride ("Beane" product) normally produced by the solution pyrolysis of di-_t_-butylberyllium etherate[2] is an amorphous solid with an absolute density of about 0.64 g/cc and a bulk density of only 0.27 to 0.35 g/cc. This relatively low density is a disadvantage in volume-limited applications. The high volumetric loadings required in the finished propellant result in formulation difficulties for maximum impulse systems.

A higher density, crystalline form of beryllium hydride was discovered at Ethyl Corporation under Air Force and ARPA sponsorship.[2] Limited quantities of this material have been produced by a high pressure-temperature treatment of lithium-doped beryllium hydride (the crystalline product denoted as "Ethylane"). Two different crystalline modifications have been identified; one is designated Phase 338-208 (from the two strongest lines in the X-ray powder pattern) and has been assigned a hexagonal structure. The second form is Phase 378-295 and probably is monoclinic. The density of both polymorphs is believed to be 0.80-0.82 g/cc. This increase in density affords a significant improvement in the range of solids loading for both solid and liquid propellants.

Crystallization of non-doped amorphous beryllium hydride under conditions of high temperature and pressure was also reported recently.[3] The same two crystalline polymorphs were obtained. However, operating temperature and pressure requirements are much higher and cycle times longer than that required for crystallization of the lithium-doped material.

The program is divided into two parts: first, an initial phase devoted to demonstrating the feasibility of a hydrostatic compaction process and to provide definition of the critical process parameters. Secondly, the most promising process is to be scaled-up to provide ten pounds of crystalline product for evaluation in propellant compositions. The overall objective is to develop a practical and economical route for pressure crystallization of beryllium hydride.

(C) <u>SUMMARY OF RESULTS</u>

The hydrostatic high pressure equipment, with a reactor volume of about 70 cc and a pressure rating of 200,000 psi, was obtained near the end of this report period, and its installation was begun. In the interim, experimental effort was spent primarily in three areas of investigation.

One study was concerned with the definition of the compaction-crystallization characteristics of high-purity, lithium-doped beryllium hydride (about 96 wt % BeH_2, 1.3 wt % Li) which represents today and probably for the near future the optimum feed composition for larger-scale densification. An improved piston-mold high pressure unit was used for this investigation, which will serve as baseline and guide for the projected hydrostatic pressure experiments. The results of this study indicate that the pressure-temperature requirements for complete crystallization of high-purity, lithium-doped BeH_2 are very similar to those earlier experienced with lesser-grade Ethylane feed material. However, it was also found that crystallization of high purity Ethylane feed apparently tends to yield polymorph distributions with relatively higher concentrations of Phase 338-208. This crystalline polymorph was produced in this latest study with densities somewhat lower than previously indicated (about 0.75-0.77 instead of 0.81-0.82 g/cc).

The other crystalline polymorph, Phase 378-295, was produced preferentially at higher pressures and temperatures, with a density approaching 0.80 - 0.82 g/cc. A few scouting experiments indicated that the polymorph distribution could be effected, by means such as seeding or pressure cycling, to substantially increase formation of the apparently denser and more thermally stable polymorph Phase 378-295 at lower, more practical P-T conditions.

No indication was found that the rate of temperature quench at normal process conditions would effect extent of crystallization or preferred polymorph. However, a rapid pressure quench at elevated temperature proved to be detrimental to the compaction-crystallization process. At a temperature of 200°C, without applied pressure, Phase 338-208 was completely destroyed (being reverted to the amorphous state) within only 5 minutes. This points out that the cycle time in a process scale-up would have to allow for a partial temperature quench (to a level of about 150-180°C) before depressurization.

The second area of activity was concerned with pre-treatment of the finely divided Ethylane feed prior to crystallization by hydrostatic compaction. In this study we discovered that an amorphous glassy form of beryllium hydride can be produced from pre-compacted feed material by fusion at elevated temperature. Ethylane feed, pre-compacted at ambient temperature at about 200 kpsi, undergoes fusion within one-half hour at about 170-200°C in the absence of applied pressure. The fused material appears to possess high surface integrity, suggesting that it could be used directly as feed in hydrostatic compaction without need for encapsulation.

A third effort was directed to a study of factors influencing the composition of beryllium hydride impurities, with the aim of further improving Ethylane feed purity. Samples of the di-t-butylberyllium etherate pyrolysis feed were found to contain 0.5-0.6 wt % t-butoxide groups. This impurity was shown to enhance the thermal stability of t-butyl groups under the normal pyrolysis conditions at 200°C. The information gained in this investigation guided successful efforts to improve operation of our Beane production unit. Attempts to further improve Ethylane feed purity through hydrogenolysis of residual alkyl groups at 5000 psi hydrogen pressure and about 200°C proved fruitless.

(C) EXPERIMENTAL AND DISCUSSION

Crystalline beryllium hydride is presently being produced in multi-pound quantities by Ethyl Corporation for evaluation in propellants. The crystalline material is prepared from lithium-doped beryllium hydride containing about 1.8 wt % lithium, added as n-butyl-lithium to the di-t-butylberyllium etherate prior to pyrolysis. Crystallization is accomplished in a 2 in. I.D. piston-and-mold unit, using a 350 ton hydraulic press as the pressure source. The operation has encountered difficulties arising primarily from mold and piston failures. Mushrooming of the piston causes it to freeze in the mold; periodic mold rupture occurs from metal fatigue. This process is considered impractical for producing large quantities of crystalline beryllium hydride, but did represent the best available means for preparing sufficient amounts for preliminary evaluation in propellant formulations.

A more practical method is needed for generating the high pressure required for crystallization. The hydrostatic compaction technique offers the advantage that pressure is applied to the material through a liquid medium so that an equal pressure is exerted in all directions. If the material to be treated is encapsulated in a metal container prior to hydrostatic compaction, one then has the analogy to the conventional piston-mold arrangement, in which the hydrostatic medium corresponds to the piston and the container to the mold. Feasibility of crystallizing Ethylane feed in a hydrostatic system has been reported by Rocketdyne.[3] Crystallization was accomplished by encapsulating the Ethylane feed in gold foil, inserting it in a pressure reactor filled with water, then pressurizing and heating the water. The efficiency of hydrostatic (or isostatic) compaction seems to be favorably high. In the metals-forming industry lower hydrostatic pressures can be employed to produce the same properties effected by ram-and-cylinder devices.

The program to be followed will employ equipment capable of generating hydrostatic pressures up to 200 kpsi. However, the goal is to define a process which will require pressures below 100 kpsi. This higher pressure unit will permit a broader definition of the pressure-temperature-time crystallization parameters. The exploratory phase of the program will be conducted with a small pressure vessel of 70 cc capacity; the production phase will make use of a larger (1000 cc) vessel.

Variables to be initially investigated are:

1. Beryllium hydride feed composition,
2. Pretreatment of beryllium hydride,
3. Crystallization parameters, and
4. Post treatments.

During the first quarter, covered in this report, the hydrostatic equipment was delivered late; therefore, only installation was begun. Consequently, major efforts were placed on the effect of feed composition and pretreatment on crystallization of beryllium hydride in improved piston-mold apparatus. Each of the topics will be covered in the following sections.

High Pressure Compaction Equipment

Hydrostatic Unit

The following hydrostatic equipment for use in this program were obtained from Harwood Engineering Co., Walpole, Massachusetts:

1 - Control panel with air operated pressure generating unit, for service to 200,000 psi

1 - Pressure vessel, 1 in. I.D. x 6 in. cavity, rated at 200,000 psi.

Photographs of the pressure control panel and pressure vessel are shown in Figure 1.

The equipment was delivered late this quarter and, while progress was made on installation of the unit in the laboratory, fabrication of safety shielding and some high pressure piping remained to be completed.

Improved Piston-Mold Unit

Most of the earlier work at Ethyl Corporation on crystallization of beryllium hydride employed a $\frac{1}{2}$ in. I.D. x 3 in. piston-mold apparatus.[4] Although this equipment performed satisfactorily for most experiments, it was limited in its rate of cooling under pressure. In order to more thoroughly investigate the temperature-pressure quench regime, an improved heating-cooling system was designed for use with the piston-mold unit. Essentially, it consisted of a cooling coil closely fitted to the outside body of the mold, and this entire unit positioned within a metal sleeve around which a 1500 watt, 110 V volt calrod heating element was wrapped. This assembly was placed in a cylindrical metal container and insulated. A $2\frac{1}{2}$ in. section of metal bellows was welded to the housing to provide continuous sealing during the compression movement of the hydraulic press. In addition, it had a gas inlet providing for a nitrogen purge of the unit during operation, and its $\frac{1}{2}$ in. thick steel bottom was bored to permit circulation of a coolant. For temperature quenching, the unit was routinely cooled with cold tap water, resulting in cooling rates of about 15°C/min. Thus, it required only 3-4 minutes to quench temperature from the usual operating level of 200°C to about 140-150°C which is below the temperature range for rapid reversion of crystalline Phase 338-208 to amorphous beryllium hydride (for comparison, complete immersion of the mold and piston into ice water still required 1.0 min. for the same quench).

Figure 1 - Control Panel, Hydraulic Pressure Generating Unit
and Pressure Vessel, for Service to 200,000 psi
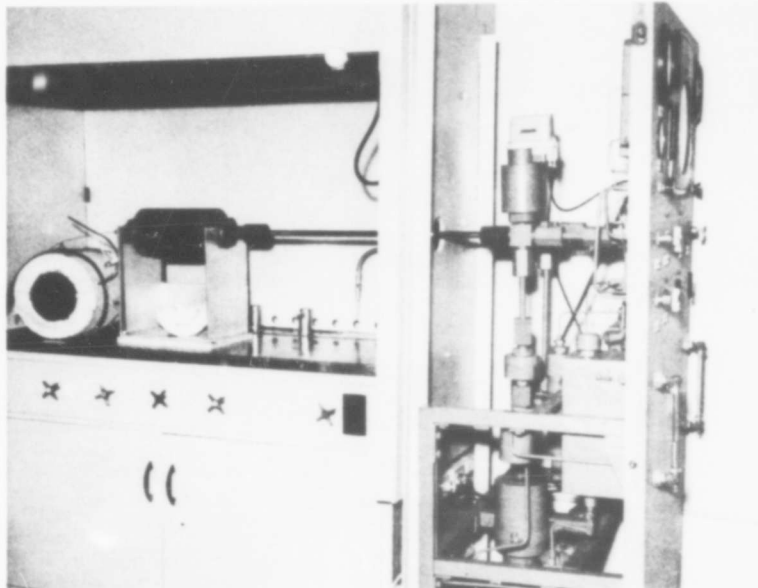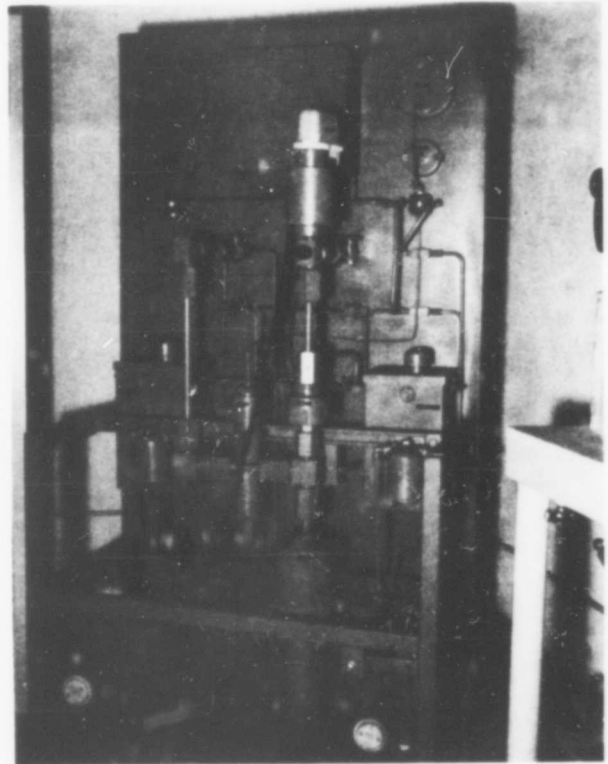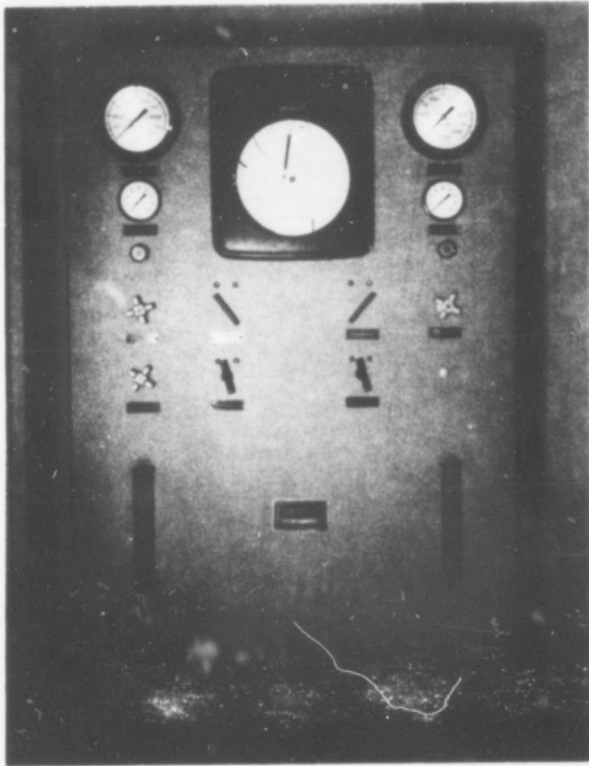
Compaction-Crystallization Studies with High Purity
Lithium-Doped Beryllium Hydride ("Ethylane")

    While awaiting installation of the high pressure hydrostatic equipment,
experimental studies began on defining the effect of Ethylane feed purity as a
variable in the densification-crystallization process. The main objective of
this study was to determine the compaction characteristics of very high purity
material.

    Previous investigations have shown that certain feed compositions can
be crystallized more readily than others, and considerable effort was directed
towards seeking and exploring additives ("dopants") which substantially lower
the pressure-temperature-time requirements for successful compaction of
beryllium hydride.

    In general, results of these previous studies indicate that the beneficial
effect of such intentionally added dopants and the effect of certain "natural"
impurities (such as beryllium metal) increases with the quantity being present.
Conversely, it might be expected that the process requirements for crystallizing
beryllium hydride might become considerably more stringent as the feed purity
is increased. This question is particularly important in view of the fact that the
performance value of beryllium hydride as a high energy fuel is highly dependent
on its purity level, and consequently, that there is much incentive to further
improve product quality. The crystallization behavior of high purity non-doped
beryllium hydride was recently studied by workers at Rocketdyne.[3] Conceivably,
however, their results could have been affected by the excessive temperatures
and times which were required for crystallization. These conditions could have
permitted trace decomposition to occur; as we have shown in earlier programs
beryllium metal in small quantities effectively lowers the pressure requirements
for beryllium hydride crystallization.

    Our current study with the piston-mold equipment serves also the purpose
of furnishing the necessary baseline for comparison with future performance of
the hydrostatic compression method. In addition, with the use of an identical
high purity Ethylane source as feed for a larger series of compaction runs, we
hoped to obtain a better definition of the densities associated with the two crystalline
polymorphs of beryllium hydride, Phases 338-208 and 378-295.

    Until recently, results of compaction-crystallization studies were often
subject to variations in feed stock composition, the effects of which on purity and
density of the compressed samples are difficult to assess. Also, on the basis of
previous experimental results it has always been assumed that the true density of
Phase 378-295 (polymorph with presumably monoclinic structure) approaches
closely 0.81-0.82 g/cc, the theoretical density of Phase 338-208 (polymorph with
hexagonal structure) as derived from X-ray diffraction data. For these reasons,
densification-crystallization experiments were preferentially evaluated by X-ray
analysis. Determination of the degree of product crystallinity appeared to be a
more meaningful measure of the outcome of compaction experiments than product
densities.

Our latest compaction experiments employed the improved $\frac{1}{2}$ in. I.D. piston-mold unit which permits use of a rapid temperature quench. The feed material primarily investigated was high purity lithium-doped pyrolytic beryllium hydride (Ethylane feed sample B459-61; 95.9 wt % BeH_2, 1.3 wt % Li) which represents one of the highest quality Ethylane feeds yet produced (impurity level of only about 2.5 - 3 wt %). In most instances the sample (about 0.4 - 0.5 g) was heated under pressure to the indicated temperature (within about 50 min. for 200°C) and, after a certain temperature holding time, quickly cooled while maintaining pressure (quench rate from 200° to 140°C was 3-4 min.). The results of these experiments are summarized in Table I. For convenience and better comparison these data will be presented again in appropriate form when being discussed or interpreted in one of the following topics of evaluation.

Effect of Process Parameters and Feed Purity on Ethylane Crystallization

The results of our compaction experiments with high purity Ethylane feed in the normal pressure-temperature-time regime (100-200 kpsi; 150-200°C) indicate that variations in Ethylane purity in the 93-96 wt % BeH_2 range (corresponding to an impurity level of 2.5 - 5.5 wt %) do not appreciably effect the P-T requirements for complete crystallization. Accordingly, a further (desirable) increase in Ethylane feed purity of about 1-2% (2.5% would be maximum) should not be expected to drastically change the reported crystallization characteristics.

As already mentioned, assessment of the effect of high feed purity upon the P-T-time requirements for successful compaction is to be based mainly on a comparison of our current results with X-ray analysis data previously obtained with lower-purity Ethylane feed. In essence, results are being compared which reflect the ease of crystallization at various sets of P-T conditions. Table II shows the range of time (in minutes) in which complete crystallization of the high purity Ethylane feed (B459-61) was obtained. The data given in parenthesis represent the results of similar compaction experiments[2,6] previously obtained with Ethylane feed of about 93-94% purity containing a comparable amount of lithium dopant.

Table II - Time Requirement (min) for Complete Crystallization of 96 Wt % Purity Ethylane Feed (data in parenthesis relate to 93-94% purity feed)

	Pressure-Temperature Conditions	
	150°C	200°C
100 kpsi	60 - ?	30 - 120
	(5 - ?)	(30 - ?; <5)
150 kpsi	5 - 30	5 - 30
	(>5)	(30 - ?; <5)
200 kpsi	5 - 60	<1
	(5 - ?)	(<30; <5)

Table I

Crystallization of High-Purity Lithium-Doped Beryllium Hydride[a]

Expt. No.	Temp., °C	Press., Kpsi	Time, min.	Product[c] Density, g/cc	Amorphous	Phase 338	Phase 378
64	150	100[g]***	60	-	100	0	0
29	200	100	5	0.67-.69	100	0	0
35[b]	200	100	5	0.68-.70	100	0	0
37	200	100	30	0.66-.67	100	0	0
54	200	100[g]*	35	0.67	80-90	5-10[i]	5-10
76	200	100	120	0.72-0.73	0	95-99	1-5
30	150	150	5	0.62-.65	100	0	0
39	150	150	30	0.69-.71	0	93-98	2-7
38	190	150	24	0.71-.73	0	95-99	1-5
28	200	150	5	0.69-.70	40-60	40-60	5
27	200	150	30	0.72-.73	0	95-99	1-5
40	150	200	5	0.69	100	0	0
20	150	200	60	0.71	0	93-98	2-7
67[h]	200	200[h]	<1	-	100	0	0
24	200	200	1	0.72-.73	0	95-99	1-5
49[d]	200	200	1	0.75	0	~50	~50
52[d]	200[e]	200	1	0.73-.75	0	80-85	15-20
34[b]	200	200	5	0.73-.74	0	95-99	1-5
25	200	200[f]	15	0.72-.73	0	95-99	1-5
21	200	200	15	0.73-.75	0	~90	~10
63	200[e]	200	30	-	0	~85	~15
48	200	200	30	0.74-.75	0	~60	~40
53	200	200[g]*	30	0.76	0	~30	~70[i]
23	200	200	60	0.74-.75	0	~90	~10
22	200	200[g]**	90	0.73	0	~85[i]	~15
46	~250[e]	200	1	0.76-.77	0	~45	~55
65	230	300-230	1	-	0	~20	~80

(a) Ethylane feed B459-61 (95.9 wt % BeH$_2$, 1.3 wt % Li)
(b) Ethylane feed B320-1 (94.5 wt % BeH$_2$, 1.8 wt % Li)
(c) As measured by sink-float method
(d) Seeded with 5.4 wt % Ethylane E166 (40% Phase 338-208, 60% Phase 378-295)
(e) Slow cooling rate (Run No. 46 and 52: 4°C/min; Run No. 63 : 86°C/hour)
(f) No pressure during cooling period
(g) During heating, pressure was alternately applied and released for 4 times with residence times each of about 4-5 min. Pressure cycling was carried out(*) before, (**) after designated temperature was reached.
(h) Sample was compacted (200 kpsi), then heated without pressure at 200°C for 35 min., and after pressing (200 kpsi) immediately cooled.
(i) Larger size crystallites as indicated by spotty X-ray diffraction pattern.

These data show that Ethylane feed samples varying in purity from about
93-?6% are crystallized in the stated P-T range at comparable rates. At 150 kpsi
and 150-200°C crystallization was complete within 5-30 minutes, while at 200 kpsi
and 200°C it occurred almost immediately. Even at pressures as low as 100 kpsi
Ethylane feed appeared to be completely crystallized at 200°C within 2 hours.
Conditions of still lower pressures and prolonged periods of time were not tested.

Effect of Process Parameters and
Feed Purity on Ethylane Crystal Morphology

Previous investigations[6] at Ethyl using Ethylane feed materials of about
93-94% purity have shown that the crystalline polymorph Phase 378-295 is
preferentially formed at relatively high pressures and temperatures (above about
200 kpsi and 200°C), while Phase 338-208 is favored at less stringent process
conditions. The results of our current compaction experiments with 96% purity
Ethylane feed, even though quite limited in number, are in good agreement with
these earlier findings. This is shown in Table III which illustrates the effect
of process conditions on the polymorph distribution.

Table III - Effect of P-T Parameters on Ethylane
Polymorph Distribution, Phase 338-208 : Phase 378-295*
(estimated distribution in %)

Pressure	Temperature (°C)				
(kpsi)	150	175	200	225	250
100	30:0	X:0	97:3 / 97:0	97:0	100:0
150	95:5 / 70:0	95:0	97:3 / 93:7	95:5	62:38
200	95:5 / X:<5	100:0	90:10 / 75:25	50:50	45:55 / 30:70
250	70:5	95:5	70:30	20:80 / 45:55	2:98
300	X:<10	63:37	60:40	23:77	5:95

*Underlined figures represent current results with high purity feed (95.9 wt % BeH$_2$,
1.3 wt % Li). All other figures represent data from an earlier study[5] using about
93-94% purity feed (1.6 wt % Li). If figures do not add up to 100%, then crystal-
lization was incomplete and the balance denotes the amount of amorphous phase.

While these particular results are well in accord, other instances should be noted in which certain comparable process conditions yield considerably higher concentrations of Phase 378-295 than indicated in Table III. Thus, Ethyl's pilot plant production, operated at 190 kpsi and 195°C, furnished Ethylane products (average composition, about 90 wt % BeH₂, 1-3 wt % Be metal, 1.6 wt % Li) which showed an average polymorph distribution of about 15-40% Phase 338-208 and 60-85% Phase 378-295. At present we can only speculate about possible causes for such discrepancies.

So far, the overwhelming majority of experimental evidence indicates that in the Ethylane crystallization process, Phase 338-208 is the polymorph first formed and that it is also the intermediate in the formation of Phase 378-295. While in the (apparently irreversible) transformation of Phase 338-208 to Phase 378-295 the conditions of pressure and temperature appear to be prime factors, other parameters such as catalysts (including seeding) or pressure and temperature cycling seem to have also a pronounced effect upon polymorph distribution. To date, however, only very few experiments have been made regarding this aspect, and no firm conclusion can be made at this time. Experimental results are listed in Table IV which also includes data pertaining to the effect of time on polymorph distribution.

Table IV - Effect of Other Process Parameters (Time, Seeding, P-T Cycling) on Ethylane Polymorph Distribution
P-T Conditions: 200 kpsi; 200°C
Ethylane Feed: B459-61 (95.9 wt % BeH₂, 1.3 wt % Li)

Expt. No.	Process Parameters		Phase Distribution (%)		
	Time (Min.)	Others	Amorph.	338	378
2080-24	1.0	-	0	95-99	1-5
52	1.0	Seeded[a]	0	80-85	15-20
49	1.0	Seeded[a]	0	~50	~50
34	5	Diff. feed[b]	0	95-99	1-5
21	15	-	0	~90	~10
63	30	Slow cooling rate[c]	0	~85	~15
23	60	-	0	~90	~10
48	30	2X compacted[d]	0	~60	~40
53	30	P-cycling before T[e]	0	~30	~70
22	90	P-cycling during T[e]	0	~85	~15

(a) Seeded with 5.4 wt % Ethylane (E-166; 40% Phase 338-208, 60% Phase 378-295)
(b) Ethylane feed B320-1 (94.5 wt % BeH₂, 1.8 Wt % Li)
(c) 86°C/hour
(d) Sample was treated by 2 separate compactions, each with similar conditions, except a rapid pressure quench at 200°C in first run.
(e) During heating pressure was alternately applied and released for 4 times with residence times each of about 5 min. In Run 53, P-cycling was completed during heat-up; in Run 22, cycling was done during holding time at 200°C.

The data in Table IV indicate that the duration of time for which Ethylane feed was heated at 200°C and 200 kpsi, exerted a small but noticeable influence on crystal phase distribution. Increase in temperature-holding times from 1 to 60 minutes were found to result in an increase of Phase 378-295 concentration from about (1-5)% to (10-15)%. One might speculate that prolonged heating times will cause trace decomposition of Ethylane to beryllium metal to occur which in turn might enhance formation of Phase 378-295. Data from our earlier programs pertaining to the effect of process parameters other than P-T conditions on Ethylane morphology are relatively scarce and give only indirect evidence that such other factors do exist. The above quoted, unexpectedly high concentrations of Phase 378-295 in Ethylane material from our pilot plant production suggests that a transformation of Phase 338-208 to Phase 378-295 might also in this case be induced and enhanced by the presence of beryllium metal (found, 1-3 wt %) and possibly other impurities.

The results of Expt. Nos. 52, 49 and 48 (see Table IV) might be interpreted by a similar consideration. Before compaction and heating, the feed materials in these cases already contained appreciable amounts of Phase 378-295, which obviously promoted crystallization by a seeding action. It may be of interest to mention that seeding of Ethylane feed with large amounts of crystalline material successfully effected crystallization merely by compaction without heating.[8] The discrepancy in phase distribution noted in Run No. 52 vs 49 might be explained by the very short process time; with somewhat longer duration of heating, more consistent results could reasonably be expected.

The technique of pressure cycling while heating the sample (see Expt. Nos. 22 and 53, Table IV) affords very striking results. This procedure was originally devised for an attempt to produce pure Phase 378-295. It has been shown[5,8] that Phase 378-295 is considerably thermally more stable than Phase 338-208, which upon heating at a temperature level of about 160-180°C at normal pressure reverts readily back to the amorphous state. Consequently it was thought that repeated pressure cycling at elevated temperature could utilize these specific properties to destroy Phase 338-208 during pressure release, and to gradually build up the concentration of Phase 378-295 by subsequent re-compaction.

The actual experimental data (Run No. 53) show that the desired result was achieved if pressure cycling was completed during heat-up of the sample, before the final compaction at 200°C was carried out. However, we feel that in this case the described reversion mechanism is not likely to be involved since temperatures during heat-up are generally below the reversion temperature level. We rather speculate that a "shearing" effect might be responsible which would facilitate a direct structural re-orientation of Phase 338-208 to Phase 378-295, similar to the effect vibration has on crystallization.

This view is supported by the results of Expt. No. 54 (see Table I), the only other run which also used pressure cycling during the heat-up period. In this case it was employed with a pressure of only 100 kpsi, but also before the

temperature of 200°C was reached and maintained for 35 minutes. It seems significant that this run yielded about 10-20% crystallinity (with presence of larger crystallites), whereas a similar experiment without pressure cycling (Run No. 37, Table I) showed no sign of crystallization. Perhaps it is also noteworthy that the partly crystallized product from Run No. 54 contained Phase 338-208 and 378-295 in about the same quantity.

We plan to check if it is of general advantage to use this pressure cycling technique, or at least lower pressures, during heat-up of the sample in order to avoid a possible "freezing" of less desirable structural orientations by high pressure. It is noteworthy that the product of Run No. 53 showed a strongly spotted X-ray diffraction pattern which indicated the presence of relatively large crystallites of Phase 378-295. This might possibly lead the way to an eventual determination of the lattice parameters of Phase 378-295 by single crystal X-ray diffraction which so far has not been done.

In Expt. No. 22 pressure cycling was carried out <u>during</u> the temperature-holding time at 200°C, and the result was quite different from that of the two other runs (Nos. 53 and 54). In this case, Phase 338-208 was preferentially formed, at exactly the ratio that would be expected from a normal run without pressure cycling. Interestingly, also for this product was the X-ray diffraction pattern indicative of formation of larger crystallites, but in this case only of Phase 338-295. In contrast to pressure cycling <u>during heat-up</u> (at lower temperatures), we prefer for the P-cycling process <u>during</u> the temperature-holding time (at 200°C) the "reversion" mechanism as a speculative interpretation of the results. Pressure cycling would in this case function merely as a method of recrystallizing Phase 338, while the formation of Phase 378 from Phase 338 (representing the inter-mediate) at maximum P-T conditions of 200°C and 200 kpsi, would still remain a relatively slow process.

In summary, our results indicate that high purity Ethylane feed, as crystallized by a simple compaction procedure at relatively short heating times, can be expected to yield a polymorph distribution with relatively high, optimum concentrations of Phase 338-208. We also have shown that process parameters other than P-T time conditions can exert a significant effect upon the distribution of the two polymorphs by substantially increasing the concentration of Phase 378-295. Up to now, available experimental data do not suffice for definite con-clusions, but they point out possible avenues for further exploration which indicate that high concentrations of Phase 378-295 could be produced, if so desired, at process conditions which normally favor Phase 338-208.

Relationship Between High Purity Ethylane Density and Polymorph Distribution

Experimental evidence from previous studies[a] indicated that crystalline beryllium hydride, regardless of its polymorph distribution, apparently has a true density of about 0.79-0.84 g/cc (as measured by liquid displacement). Measure-ments by the sink-float method generally gave somewhat lower values, about

0.77-0.80 g/cc. In addition, a theoretical density of 0.82 g/cc was calculated for the crystalline polymorph Phase 338-208 from a single-crystal electron and X-ray diffraction analysis. Also, on the basis of theoretical considerations, it was concluded that the true density of Phase 378-295 would closely approach the same value.

Surprisingly, and partly in contrast to this assumption, the current study indicates that the densities of the two crystalline polymorphs may differ more widely from each other, and that the density of Phase 338-208 is probably lower than previously thought. The results of these latest compaction experiments, which were carried out with a single source of high purity feed material, are listed in Table V.

Table V - High Purity Ethylane[a] Densities and Phase Distributions

Expt. No. 2080-	Product[b] Density, g/cc	X-Ray Diffraction Data, Estimated Concentrations, %		
		Amorph.	Phase 338	Phase 378
39	0.69-.71	0	93-98	2-7
20	0.71	0	93-98	2-7
38	0.71-.73	0	95-99	1-5
24, 25, 27, 76	0.72-.73	0	95-99	1-5
34[a]	0.73-.74	0	95-99	1-5
21	0.73-.75	0	~90	~10
22	0.73	0	~85	~15
52	0.73-.75	0	80-85	15-20
48	0.74-.75	0	~60	~40
49	0.75	0	~50	~50
46	0.76-.77	0	~45	~55
53	0.76	0	~30	~70

(a) All compaction runs but one (No. 34) used Ethylane feed B459-61
    (95.9 wt % BeH_2, 1.3 wt % Li) - Expt. No. 34 used
    (94.5 wt % BeH_2, 1.8 wt % Li)
(b) As determined by sink-float method

These data show that Ethylane products comprised almost exclusively of the crystalline polymorph Phase 338-208 (estimated concentrations were between 93-99%) gave, in remarkable accord, "sink-float" densities of about 0.71-0.73 g/cc, while samples containing increasing concentrations of the other polymorph, Phase 378-295, showed a corresponding increase in their densities. So far, however, concentration of Phase 378-295 in a given sample did not exceed the 70% level, so that the density of this polymorph in its pure state can presently be estimated only by extrapolation. Based on the relatively few, available data, a "sink-float"

density of approximately 0.77-0.78 g/cc seems to be indicated for Phase 378-295, which in fact is in very good agreement with the earlier findings. Since Phase 378-295 was found to represent the polymorph preferentially formed at higher P-T conditions, it appears quite reasonable that this high pressure phase should have a higher density than Phase 338-208.

The discrepancy in the density designation for Phase 338-208 could be explained by the fact that earlier investigations often lacked a common baseline. At the time Ethylane feed was often relatively low in purity, varying widely in composition, and available quantities were in many cases too small to suffice for more than a few experiments. Furthermore, although the effect of impurities on product densities has qualitatively been taken into consideration, we still know too little to assess this significant factor satisfactorily. Therefore, at the present time, we hesitate to draw any definite conclusions. For a better definition, we would need additional data on the effect of impurities on product density and a more complete evaluation of the difference between density measurements made by liquid displacement and by the sink-float method.

Effect of Rapid Temperature and Pressure Quench on High Purity Ethylane Compaction

The majority of the reported compaction experiments employed a temperature quench rate of about 17°C/min. This approaches the maximum cooling rate attainable for a piston-mold unit of the described scale, and probably also for any practical hydrostatic pressure equipment. The results of this study, as compared with experiments using lower cooling rates, of the order of 2-4°C/min, all indicate that rapid temperature quench has no significant effect on the extent of crystallization or the preferred polymorph.

Of more practical importance is the definition of the effect which a rapid quench of pressure has on the compaction-crystallization of high purity Ethylane at elevated temperature. The behavior of the compacted, crystalline mass during rapid depressurization and subsequent cooling affects the cycle time and handling techniques involved in process scale-up. If the reactor temperature during product discharge could remain relatively high, appreciable savings in cycle time would be realized.

To probe this effect with high-purity Ethylane feed, several experiments were conducted in which feed samples were compacted and heated for 30 minutes at certain conditions of temperature and pressure; the pressure then being released for 5 minutes before the sample was rapidly cooled. The results of these tests are summarized in Table VI.

Table VI - Effect of Rapid Pressure Quench on Crystallization of
High Purity Lithium-Doped Beryllium Hydride[a]

Expt. No. 2080-	Test Conditions Temp., °C	Press., Kpsi	Product[d] Density, g/cc	X-Ray Diffraction Data Est. Concentrations, % Amorphous	Phase 338	Phase 378	Remarks
-32	160	150	0.65	~80	~20	0	Glassy product
-33[b]	200	100	<0.01	40-60	40-50	0	Crumbles easily
-26	200	200	0.62	~90	0	~10	Glassy product
-45[e]	200	200	<0.61	100	0	0	Glassy product
-41	210	50	<0.61	100	0	0	Hard, but not glassy
-31	210	100	0.62-.63	100	0	0	Glassy product
-25[f]	200	200	0.72-.73	0	95-99	1-5	Fractures easily
-48[g]	220	200	0.74-.75	0	~60	~40	Crumbles easily

(a) Ethylane feed B459-61 (95.9 wt % BeH_2, 1.3 wt % Li)

(b) Ethylane feed B320-1 (94.5 wt % BeH_2, 1.8 wt % Li)

(c) All samples were heated at the indicated temperature and pressure for 30 min.
Then they were heated an additional 5 minutes without pressure before they
were rapidly cooled. However, note deviations in procedure for Expt. Nos.
25, 45, and 48.

(d) As determined by sink-float method.

(e) Heating period without applied pressure was extended to a total of 30 min.

(f) Sample was heated for only 15 min. before pressure and temperature were
simultaneously quenched.

(g) Product sample was re-compacted at 200°C and 200 kpsi for 30 min. in the
standard manner.

These data are in accord with earlier investigations[5,6] which indicated that Phase 338-208 readily reverts to the amorphous state when heated to elevated temperatures (above 160-180°C) without applied pressure. Thus, Run No. 32 shows, as was expected, that reversion of this crystalline polymorph proceeded at a relatively slow rate at 160°C. A substantial quantity of Phase 338-208 still survived after 5 minutes of heating. Somewhat as a surprise, however, we found that the rate of Phase 338-208 reversion, even at a temperature of 200°C, was so slow that the crystallinity of a sample which was rapidly cooled immediately after depressurization (Run No. 25, cooling rate was about 17°C/min.) was not affected. It may also be significant that an Ethylane sample with only a slightly lower purity (B320-1, 94.5 wt % BeH$_2$) retained an appreciable amount of Phase 338-208 even after heating for 5 minutes at 200°C (Run No. 33). Extended heating periods (30 minutes) at about 200°C without applied pressure, completely destroyed Phase 338-208 and any small amount of Phase 378-295 which might have been present (Run No. 45).

A generally similar behavior was observed for Phase 378-295 which had already been characterized[5,6] as the more thermally stable polymorph of beryllium hydride. In Run No. 26, Phase 378-295 was found, after heating at 200°C for 5 minutes, to still be present at the expected, original concentration of about 10% (as indicated by comparison with the untreated products of Run Nos. 21 and 23 in Table I).

As observed in an earlier study[6], the densities of partly or completely reverted samples were found to be lower (in general about 0.61-0.63 and lower) than that of untreated Ethylane feed. It seems reasonable to assume that this volume expansion was caused by small amounts of thermally evolved hydrogen.

Interestingly also, most of the affected samples were discharged in the form of gray, hard, glassy pellets representing a special physical state of amorphous beryllium hydride. This material could be shattered into sharp, compact, translucent fragments. It was readily transformed to the usual crystalline forms when compacted and heated in the standard manner (Expt. No. 48).

In summary, the relatively few scouting experiments indicate that the crystalline polymorph Phase 338-208 does rapidly revert to the amorphous state when heated at a temperature level of 200°C. However, the rate seems slow enough to possibly permit a pressure quench without degrading the sample, if temperature can be dropped within a very short time to a level below about 160°C. Translated into terms of a practical hydrostatic process, this teaches that a rapid quench of pressure and temperature might be acceptable and feasible if cold hydraulic fluid could be pumped into the reactor during depressurization.

Pre-Treatment of High Purity Ethylane Feed

The discovery that a glassy state of beryllium hydride can be produced merely by heating a pre-compacted sample at elevated temperature, without pressure being applied, prompted us to explore this phase transformation more fully, for possible application as pre-treatment for Ethylane feed. The glassy, amorphous material appears to possess high surface integrity, which suggests that it could be used directly as feed in hydrostatic compaction without need for encapsulation.

The "fusion"* of finely divided, amorphous beryllium hydride to a transparent, glassy mass has been investigated in earlier programs.[47] However, only un-doped beryllium hydride was studied at the time. Temperatures of about 160-180°C as well as the application of about 10 kpsi pressure, were found necessary for fusion of this material.

To define the conditions for producing glassy, amorphous Ethylane feed, we conducted a series of experiments using the following sequence of operations:

1. Compaction at ambient temperature,
2. Release of pressure, and
3. Heating to 150-200°C.

Operating conditions and experimental results for this series of runs are given in Table VII.

The products obtained were all amorphous, fused, rock-like pellets. Two types of products were formed - the desired glassy solid and a dull, hard material. It appears that higher temperatures, higher pellet compaction pressures, and longer heating times favor formation of the glassy product. The dull, non-glassy material seems to represent its precursor in the sintering process. In accord with this is the observation that the glassy materials tend to be darker in color, indicating that formation of beryllium metal in these samples is somewhat more pronounced than in the non-glassy products. The measured densities, generally in the range of 0.63-0.65 g/cc, do not distinguish between the two forms. Insufficient analytical data are available at present to establish any difference in composition. Hopefully, both types might be useful as feed for crystallization by hydrostatic compaction. However, there was no evidence that the fused material would crystallize more readily in a standard compaction run than the original, finely divided Ethylane feed (Expt. No. 67).

It is noted that the product density (Run No. 61) was not significantly increased by subsequent compaction at 30-40°C, and 200 kpsi after one hour.

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*This process might more accurately be denoted as "sintering" since fusion, in the sense of melting, does not seem to be involved.

Table VII – Fusion Pre-Treatment of High Purity Ethylene Feed^d

Expt. No. 2080-	Test Conditions			Product^d Density (g/cc)	X-ray Diffraction Data Concentration %		Product Appearance^h	
	Pressure^b (Kpsi)	Temp.^c (°C)	Time^c (min.)		Amorphous	Crystalline	Color	Consistency
-56	150	155	35	0.65	100	0	X	0
-58	150	200	35	-	100	0	X	0
-55	200	155	35	0.65-.70	100	0	XX	0o
-59	200	175	35	0.64	100	0	XXX	000
-51e	200	185	1	0.63-.65	100	0	x	0o
-57	200	200	5	0.63-.64	100	0	XX	00
-60	200	200	15	-	100	0	X	0o
-42	200	210	35	0.63	100	0	XXx	00
-61f	200	200	35	0.64	100	0	XX	0o
-67g	200	200	35	-	100	0	X	Micaceous

(a) Ethylene feed B459-61 (95.9 wt % BeH$_2$, 1-3 wt % Li)
(b) Pellet compaction at ambient temperature
(c) At atmospheric pressure
(d) As measured by sink-float method
(e) Seeded with 5.4 wt % Ethylane E-166 (40% Phase 338-208, 60% Phase 378-295).
(f) Sample was subsequently pressed at 200 kpsi and 30-40°C for 60 minutes
(g) Sample was subsequently pressed at 200 kpsi; 200°C and immediately cooled while maintaining pressure
(h)   X = slightly gray
     XX = light gray
    XXX = medium gray

x (or o) denotes intermediate classification

  0 = very hard, dull
 00 = very hard, semi-glassy
000 = very hard, glassy

Beryllium Hydride Feed Composition Studies

Certain beryllium hydride compositions are known to be more susceptible to compaction-crystallization than others. Additives such as lithium hydride are effective in significantly reducing pressure requirements. Beryllium metal produced in situ appears to function as a crystallization catalyst. On the other hand, little or nothing is known about the effect of process-inherent impurities, such as alkoxides, hydroxide, residual alkyl groups, etc. on ease of crystallization. Assessment of the effect of these impurities and of purposely added dopants on beryllium hydride crystallization process parameters is the primary aim of this phase of the program.

As a rule, investigation of the behavior of impurities in any material should involve, as a base-line, the material in its highest purity. Non-doped beryllium hydride, as presently produced, is available in purities of only 95-97 wt %. Up to about 2 wt % of the impurities are ethyl and ethoxide groups, believed to arise from ether-cleavage during pyrolysis, and probably cannot be minimized much further. However, it should be possible to reduce the amount of other impurities, e. g., butyl, butoxide and other oxygenated groups, by scrutinizing the sources of their introduction in the process. Elimination of impurities through chemical reaction represents another possibility as discussed below.

It is noteworthy that information obtained in this study guided successful efforts to improve operation of our Beane production unit. For the first time, an Ethylane feed material was produced with an impurity level of only about 2.5 wt %. A portion of this material is being used as high-purity feed in study of beryllium hydride crystallization parameters.

Effect of Alkoxide Impurities in Pyrolysis Feed on Beryllium Hydride Purity

Samples of the di-t-butylberyllium etherate pyrolysis feed were analyzed and found to contain 0.5-0.6 wt % t-butoxide. This concentration of t-butoxide would account for about 2 wt % impurities in the beryllium hydride product, assuming it decomposed to oxide or hydroxide. The fate of this material during the pyrolysis reaction, however, has never been investigated.

To study the effect of t-butoxide impurities on product purity, samples of di-t-butylberyllium etherate feed were prepared which contained varying amounts of t-butoxide. They were synthesized by the following reaction with t-butanol:

$$(t\text{-Bu})_2Be \cdot OEt_2 + t\text{-BuOH} \rightarrow t\text{-BuBe}(O\text{-}t\text{-Bu}) + C_4H_{10} + Et_2O$$
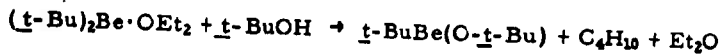
Reaction employing a 1:1 stoichiometry of the reactants yielded a product which was a crystalline solid at room temperature. A preliminary attempt to purify this material by vacuum sublimation resulted in some disproportionation:

$$2\ t\text{-BuBe}(O\text{-}t\text{-Bu}) \rightarrow (t\text{-Bu})_2Be + Be(O\text{-}t\text{-Bu})_2$$
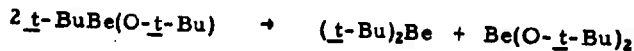
The crystalline sublimate proved to be pure beryllium di-t-butoxide (Be: calcd., 5.81 wt %; found, 5.81 wt %).

Pyrolysis of the alkoxide-enriched feed samples gave, under the usual conditions at 200°C, the following results. A pyrolysis feed containing 7.0 mole % Be(O-t-Bu)$_2$ yielded a beryllium hydride product with 26.3 wt % Bu$_2$Be (which represents 1.7 mole % of the original beryllium alkyl complement). A feed containing 13.0 mole % Be(O-t-Bu)$_2$ gave a product with 17.3 wt % Bu$_2$Be (representing 2.6 mole % of the original beryllium alkyl), while an almost pure feed gave a product containing only 1.1 wt % Bu$_2$Be. It was further found that the compound t-BuBe(O-t-Bu) retained about half its butyl groups after pyrolysis to give a completely oil-soluble product.

These results give conclusive evidence that butoxide impurities, and probably alkoxides in general, in the di-t-butyl beryllium etherate feed greatly enhance the thermal stability of butyl groups. Thus, alkoxides in the pyrolysis feed are detrimental to beryllium hydride purity not only because they themselves contribute impurities but also enhance the level of residual alkyl groups in the product.

Attempted Upgrading of Beryllium Hydride Purity by Hydrogenolysis

Impurities in the form of various beryllium alkyls, e.g. ethyl, propyl and butyl, contribute about 2-3 wt % to the usual pyrolytic beryllium hydride product. The effect of these bulky impurities on Ethylane crystallization parameters is not known, but it would be helpful to find out if they are detrimental. Hydrogenolysis appears to be the best choice for eliminating alkyl groups without the hazard of over-pyrolysis to beryllium metal.

Earlier attempts[7,8] to improve the purity of pyrolytic, non-doped beryllium hydride by hydrogenolysis of residual alkyl groups were essentially unsuccessful. Treatment with 5000 psi hydrogen pressure at 175-185°C for 18 hours proved ineffective.

These negative results did not discourage us to try again, since there was reason to hope that (lithium-doped) Ethylane feed might be more receptive towards hydrogenolysis. Two beryllium hydride samples, an unexposed Ethylane feed material (B459: 96.3 wt % BH$_2$, 1.3 wt % LiH) and an unexposed undoped product (B459: 92.8 wt % BeH$_2$, 3.80 wt % beryllium alkyls) were subjected to 5000 psi hydrogen pressure at about 200°C for 1-2 hours. The undoped material was employed as produced in Bayol 35 slurry, and the Ethylane feed was suspended in toluene. Analysis of the recovered solids gave essentially identical results before and after hydrogenolysis. Evidently, the treatment was not sufficiently severe to effect detectable reduction in product alkyl content. However, the treatment did alter physical properties of the Ethylane feed. The bulk density of this material increased from 0.10 g/cc to 0.17 g/cc; that of the undoped beryllium hydride was unchanged (0.28 g/cc).

Extraction of alkyl impurities from unexposed Ethylane feed was also attempted unsuccessfully. Treatment with hot toluene at 85°C for one hour effected no reduction in the alkyl group content.

(C) PLANS

Installation of the Harwood hydrostatic equipment and of safety shielding will be completed. A heating-cooling system for the high pressure vessel are being designed and fabricated. After testing of unit operation and high pressure fluids, efforts will be primarily devoted to process parameter studies to define optimum hydrostatic compaction conditions. Results of these experiments will be used to determine if changes in feed composition will be needed to further lower process pressure-time requirements, and they will also be employed in evaluation of process scale-up. In addition, techniques for pre-treatment and encapsulation of Ethylane feed for hydrostatic compactio₁ will be further explored.

/meb

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13. ABSTRACT (C) Ultra-high pressure hydrostatic equipment was obtained for use in BeH_2 crystallization studies. During its installation the crystallization of high-purity Li-doped BeH_2 (96 wt % BeH_2, 1.3 wt % Li) was investigated using an improved design piston-mold apparatus. The high purity feed material tended to give a product with relatively high concentrations of crystalline Phase 338-208 and densities in the range 0.75-0.77 g/cc. As the pressure and temperature was increased, Phase 378-295 formed preferentially, as expected. Its density approached a value of 0.80-0.82 g/cc. Rate of temperature quench under pressure had no effect on extent of crystallization or polymorph distribution. On the other hand, a rapid pressure quench at elevated temperature is detrimental to the crystallization process. It was found that amorphous BeH_2 can be prepared in a fused, glassy state by pre-compaction, then heating without pressure to 170-200°C.

(C) Investigation of impurities in BeH_2 showed that the presence of butoxide groups in the pyrolysis feed, di-$\underline{t}$-butylberyllium etherate, enhanced the thermal stability of the $\underline{t}$-butyl groups. This information aided the production of the highest purity Li-doped BeH_2 obtained to date. Attempts to improve purity even further by hydrogenolysis of residual alkyl groups proved unsuccessful.

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